

Signature of surface states on NMR chemical shifts: A theoretical prediction

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We show with an *ab initio* calculation that electronic surface states have a strong effect on NMR chemical-shift spectra. For the hydrogen-chemisorbed diamond (111) surface, we find that the atomic layers close to the surface experience a variation of the chemical shift, which is proportional to the density of empty surface states. This effect could be used as a direct probe of the surface-state density profile, by measuring experimentally the NMR chemical shift resolved for each atomic layer. [S0163-1829(99)00523-8]

In the bulk of a crystal, as a general consequence of lattice periodicity, the electronic states are extended. At a surface however, the translational symmetry of the crystal is broken, and localized electronic states, which are forbidden in the bulk, can exist. These surface states decay exponentially from the surface into the bulk, and play an important role in the electronic, chemical, and structural properties of the surface. They can be detected by surface-sensitive experimental techniques, e.g., with x-ray photoemission spectroscopy, ultraviolet photoelectron spectroscopy, or scanning tunneling microscopy. However, to our knowledge, only indirect experimental observations of the surface states' decay have been reported.¹ In this work, we present an *ab initio* calculation of the ¹³C nuclear magnetic resonance (NMR) chemical shifts of a diamond surface, using a recent theory developed for condensed-matter systems.² In the atomic layers close to the surface, we find surprisingly strong variations of the chemical shift, which are proportional to the probability density of an unoccupied surface state decaying into the bulk. Using this effect, it would be possible to measure directly the decay length of the surface state with NMR. We illustrate the impact of surface states on the NMR chemical shifts for an ideal flat surface, however, we expect that a similarly strong effect would occur also for different geometries, e.g., in nanoclusters, or zeolites, whenever surface states are present.

The relevance of our theoretical findings is further enhanced by recent experimental advances in surface NMR. To study surfaces with NMR, one needs to selectively enhance the signal from surface atoms. This has been accomplished, e.g., using optically pumped hyperpolarized gases. The NMR signal is proportional to the population difference in nuclear spin levels. At thermal equilibrium, this difference is usually less than 1 in 10⁵, but with optical pumping, it is possible to reach values that are close to unity. These techniques have been used to increase the NMR signal of ¹²⁹Xe in the gas and solid phases,³ or adsorbed on surfaces.⁴ Via cross polarization, the ¹²⁹Xe polarization can be transferred to other nuclei, such as ¹H or ¹³C.⁵⁻⁸ In the case of ¹²⁹Xe adsorbed

on a surface, the polarization is preferentially transferred to the nuclei close to the surface, whose signal is enhanced by many orders of magnitude.^{6,7} Moreover, one can probe nuclei at different distances from the surface by changing the contact time, and thereby the penetration depth of the spin polarization.⁷

A uniform, external magnetic field **B**_{ext} applied to a sample of matter induces an electronic current density **J**(**r**), which gives rise to a nonuniform-induced magnetic field **B**_{in}(**r**)

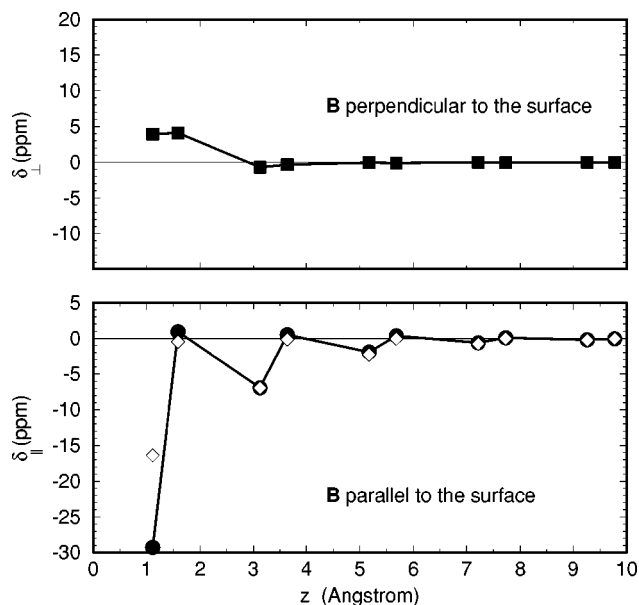


FIG. 1. The deviations of the chemical shift from the bulk value, $\delta_{\parallel}(z)$ (circles) and $\delta_{\perp}(z)$ (squares) are plotted for each C layer as a function of the distance z from the H layer. We also plot $-\rho(z)$ (diamonds), where $\rho(z)$ is the square amplitude of the surface state at the Γ point, integrated over an atomic sphere centered at each C site. The scale for ρ is chosen in such a way that, at the third layer, $-\rho(z)$ and $\delta_{\parallel}(z)$ coincide. Notice the close agreement between the two quantities. The lines are guides for the eye.

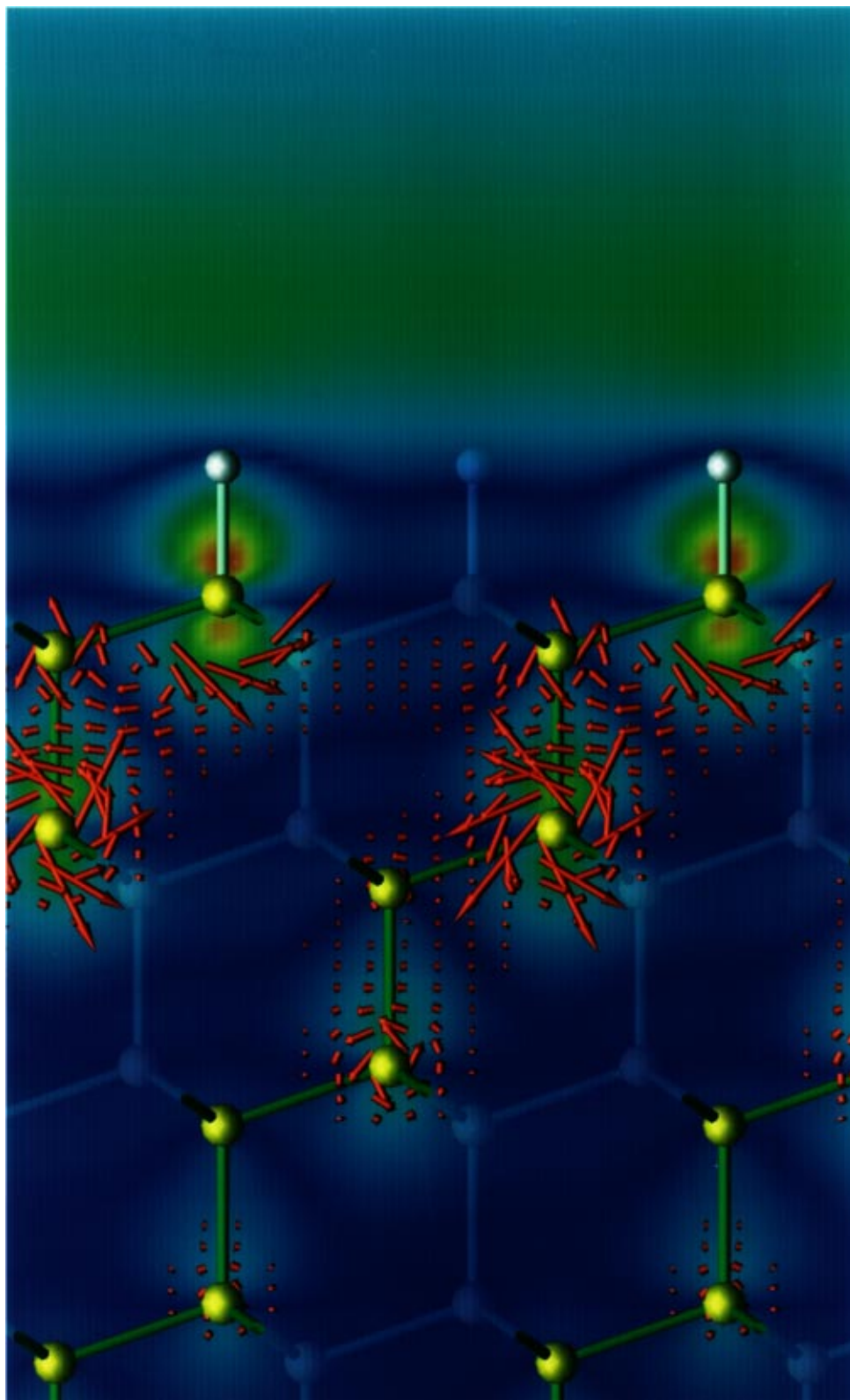


FIG. 2. (Color) Current density induced by an external magnetic field \mathbf{B}_{ext} parallel to the surface in the $(11\bar{2})$ direction (coming out of the page). We show the current density in the $(1\bar{1}0)$ plane containing the H atoms. We plot the difference $\Delta\mathbf{J}(\mathbf{r})$ between the slab and the bulk $\mathbf{J}(\mathbf{r})$. We do not plot $\Delta\mathbf{J}(\mathbf{r})$ above the top C layer, which experiences a different chemical environment since it is bonded to the H layer. The color coded density plot visualizes the square modulus of the surface state at the Γ point. Blue corresponds to low and red to high density. One can recognize the characteristic p_z shape of this state, which leads to the different behavior of $\delta_{\perp}(z)$ and $\delta_{\parallel}(z)$ shown in Fig. 1. Notice that $\Delta\mathbf{J}(\mathbf{r})$ is larger around the atoms on which the surface state resides.

$$\mathbf{B}_{\text{in}}(\mathbf{r}) = -\tilde{\sigma}(\mathbf{r})\mathbf{B}_{\text{ext}}. \quad (1)$$

Here, $\tilde{\sigma}(\mathbf{r})$ is the chemical shift tensor, which is measured at the nuclear positions by NMR.

The amplitude of $\mathbf{B}_{\text{in}}(\mathbf{r})$, even deep inside the bulk, depends on the shape of the sample and on the orientation of the external magnetic field. This effect is well known from classical magnetostatics, and is a signature of macroscopic

surface currents.⁹ As a consequence, the asymptotic bulk value $\sigma(\text{bulk})$ of the shift is different if the external field is aligned parallel or normal to the surface. We are interested here in the *microscopic* surface effects, and therefore focus on the deviation from these asymptotic bulk values at a distance z below the surface,

$$\delta_{\perp}(z) = \sigma_{\perp}(z) - \sigma_{\perp}(\text{bulk}),$$

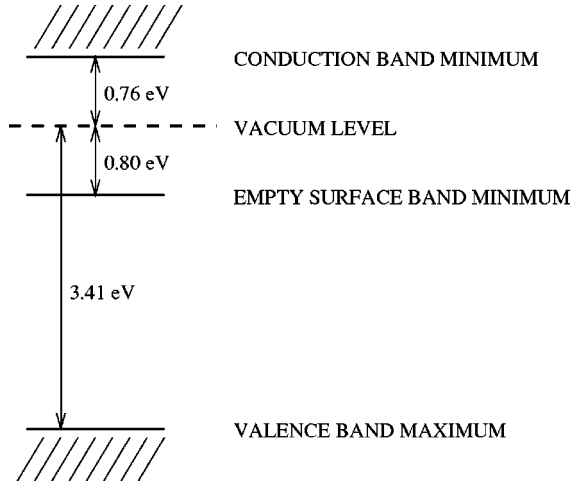


FIG. 3. Positions of the bulk and surface bands with respect to the vacuum level, computed within DFT-LDA.

$$\delta_{\parallel}(z) = \sigma_{\parallel}(z) - \sigma_{\parallel}(\text{bulk}), \quad (2)$$

where σ_{\perp} and σ_{\parallel} are the diagonal component of $\vec{\sigma}$ in the directions normal and parallel to the surface, respectively.¹¹

We now consider a particular surface, which is the ideal, hydrogen-terminated (111) surface of diamond, C(111):H. In our calculation, we model the surface using a repeated slab geometry, and we describe the electronic structure within density-functional theory in the local-density approximation (DFT-LDA).¹² We compute $\sigma_{\perp}(z)$ and $\sigma_{\parallel}(z)$ in the slab, and $\sigma_{\perp}(\text{bulk})$ and $\sigma_{\parallel}(\text{bulk})$ in bulk diamond crystal following Ref. 2. In Refs. 15 and 2, we have shown the excellent agreement of the present theory with the experimental data for various carbon systems.

The results of our calculation for the slab are presented in Fig. 1, where for each C layer we plot $\delta_{\parallel}(z)$ and $\delta_{\perp}(z)$ as a function of the distance z from the H layer. With increasing z into the crystal, the shift approaches the bulk value, and $\delta_{\parallel}(z)$ and $\delta_{\perp}(z)$ converge to zero.⁹ As Fig. 1 shows, $\delta_{\perp}(z)$ is positive, i.e., diamagnetic, and decays rapidly. When the field is parallel to the surface, the results are different and quite unexpected. We find that δ_{\parallel} is negative, i.e. paramagnetic, and decays to zero much more slowly. Even five C layers deep into the bulk, δ_{\parallel} is still -1.9 parts per million (ppm), a magnitude that can be detected experimentally. The large δ_{\parallel} for the subsurface layers *cannot* be explained by a structural relaxation mechanism, since just the first C layer relaxes significantly. We also note that δ_{\parallel} of the even layers is essentially zero, and only the odd layers show a slowly decaying δ_{\parallel} . Finally, at the first layer, the change in the isotropic shift $\delta = (2\delta_{\parallel} + \delta_{\perp})/3$ is -18.9 ppm. This paramagnetic shift is contrasted by trends observed in saturated hydrocarbons and in amorphous carbon, where a replacement of a C-C single bond by a C-H bond moves the isotropic shift by between $+2$ and $+13$ ppm,^{15,16} i.e., in the opposite direction.

To understand these surprising results, we consider the current density induced by an external magnetic field parallel to the surface. To isolate the effect of the surface, we plot in Fig. 2 the difference $\Delta\mathbf{J}(\mathbf{r})$ between the slab and the bulk

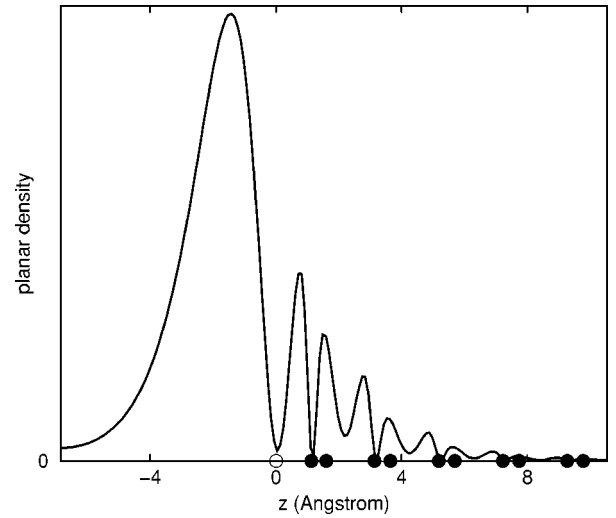


FIG. 4. Density of the lowest unoccupied surface state at the Γ point. The planar average density is plotted as a function of the distance from the H plane. The positions of the H- and C-atom planes are indicated with open and filled circles, respectively.

current density.¹⁷ From the figure we see that $\Delta\mathbf{J}(\mathbf{r})$ is localized on circular orbits around the atoms. Moreover, we find $\Delta\mathbf{J}(\mathbf{r})$ to be negligible on all the odd layers, in coincidence with a vanishing $\delta_{\parallel}(z)$. These observations indicate that $\delta_{\parallel}(z)$ for a given atom is mostly determined by induced currents around that same atom.

The trends observed for $\delta_{\perp}(z)$, $\delta_{\parallel}(z)$, and $\Delta\mathbf{J}(\mathbf{r})$ are related to the electronic structure of the surface. Experimentally, the C(111):H surface exhibits a negative electron affinity,¹⁸ i.e., the conduction-band minimum is found to be 0.7 eV above the vacuum level. DFT-LDA reproduces this property.¹⁹ In our calculation, the conduction band minimum and the valence-band maximum are 0.76 eV above and 3.41 eV below the vacuum level, respectively (the DFT-LDA fundamental gap being 4.17 eV). Furthermore, we find a nondegenerate, empty surface-state band with a minimum at the Γ point of the Brillouin zone, 0.80 eV below the vacuum level. No occupied surface states are present. These results are depicted in Fig. 3. The plane in which the surface-state density reaches its largest value is *not* located on a surface atom, but in the vacuum, 1.4 Å away from the H plane as shown in Fig. 4. Indeed the surface band originates from vacuum free-electron states that are attracted by the tail of the potential near the surface. These kinds of surface states are a general feature of negative electron affinity surfaces, and are also observed in BN graphitic sheets.²⁰

To understand the role of the surface states, we analyze the chemical shift by partitioning it into a diamagnetic and a paramagnetic term,¹⁶ $\sigma_{\hat{\mathbf{n}}}^d = \sigma_{\hat{\mathbf{n}}}^d + \sigma_{\hat{\mathbf{n}}}^p$, where $\sigma_{\hat{\mathbf{n}}}$ is the diagonal element of the tensor $\vec{\sigma}$ in the direction $\hat{\mathbf{n}}$, and

$$\sigma_{\hat{\mathbf{n}}}^d = \frac{e^2}{mc^2} \sum_i^{\text{occ}} \left\langle \psi_i \left| \frac{r^2 - (\mathbf{r} \cdot \hat{\mathbf{n}})^2}{r^3} \right| \psi_i \right\rangle \quad (3)$$

$$\sigma_{\mathbf{n}}^{\text{p}} = -\frac{2e^2}{m^2c^2} \sum_i^{\text{occ}} \sum_j^{\text{emp}} \frac{\langle \psi_i | \hat{\mathbf{n}} \cdot \mathbf{L} | \psi_j \rangle \langle \psi_j | r^{-3} \hat{\mathbf{n}} \cdot \mathbf{L} | \psi_i \rangle}{\varepsilon_j - \varepsilon_i}. \quad (4)$$

Here, $|\psi_k\rangle$ are the eigenstates of the Hamiltonian for the electrons with eigenenergies ε_k , the indices i and j run over the empty and occupied states, respectively, and \mathbf{r} and \mathbf{L} are the position and the angular momentum operators relative to the nucleus for which σ is computed.²¹ The diamagnetic term $\sigma_{\mathbf{n}}^{\text{d}}$ is always positive, whereas $\sigma_{\mathbf{n}}^{\text{p}}$ is usually negative. The presence of empty surface states in the gap increases the paramagnetic term $\sigma_{\mathbf{n}}^{\text{p}}$, since the surface states lie below the bulk conduction band, and hence the energy denominators in Eq. (4) become smaller. In particular, for the extra surface-state contributions, the numerator of Eq. (4) would be roughly proportional to the square amplitude of the surface states on the atomic site.²¹ The diamagnetic term $\sigma_{\mathbf{n}}^{\text{d}}$, which depends on occupied orbitals only, is not affected by empty surface states.

For illustration, we single out the state at the Γ point, $|\psi_{\text{surf}}^{\Gamma}\rangle$, which has the lowest energy, and should have the strongest effect on $\sigma_{\mathbf{n}}^{\text{p}}$ according to Eq. (4). In Fig. 2, we show as a color-coded density plot the square modulus of $|\psi_{\text{surf}}^{\Gamma}\rangle$. The change in current density $\Delta\mathbf{J}(\mathbf{r})$ is indeed larger where the surface state prevails. In Fig. 1 we plot $-\rho(z)$,

where $\rho(z)$ is the integral of the square amplitude of $|\psi_{\text{surf}}^{\Gamma}\rangle$ over an atomic sphere of radius 0.42 Å, centered at each C site. The scale for ρ is chosen in such a way that, at the third layer, $-\rho(z)$ and $\delta_{\parallel}(z)$ coincide. The close agreement between $-\rho(z)$ and $\delta_{\parallel}(z)$ indicates that δ_{\parallel} is indeed proportional to the square amplitude of the surface state. The agreement is not perfect for the first C layer, which experiences a different chemical environment since it is bonded to the H layer. Finally, because of the symmetry of the C(111):H surface, the expression $(\hat{\mathbf{n}}_{\perp} \cdot \mathbf{L})|\psi_{\text{surf}}^{\Gamma}\rangle$ in Eq. (4) vanishes.²² This explains why the surface state does not contribute to $\sigma_{\mathbf{n}}^{\text{p}}$ if the field direction $\hat{\mathbf{n}}$ is perpendicular to the surface.

In conclusion, we have shown that the presence of electronic surface states has a strong impact on the NMR chemical shift of atoms near the surface. Unoccupied surface states cause a paramagnetic deshielding proportional to their square amplitude. This effect could be used as a means to measure the spatial extent of surface states.

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⁹In classical magnetostatics, the surface current is $\mathbf{K} = c\chi\mathbf{B}_{\text{ext}} \times \hat{\mathbf{n}}_{\perp}$, where c is the speed of light, $\hat{\mathbf{n}}_{\perp}$ is the outwardly directed normal to the surface, and χ is the macroscopic magnetic susceptibility (Ref. 10). For a flat surface, $K=0$, if \mathbf{B}_{ext} is normal to the surface, and $K=c\chi B_{\text{ext}}$, if the field is parallel. As a result, in the bulk far from the surface, the shift differs from that of the spherical sample (σ_{sp}) which is the standard reference; $\sigma_{\perp}(\text{bulk}) = [\sigma_{\text{sp}}(\text{bulk}) + \frac{8}{3}\pi\chi]$, and $\sigma_{\parallel}(\text{bulk}) = [\sigma_{\text{sp}}(\text{bulk}) - \frac{4}{3}\pi\chi]$. It is an important consistency check for our atomic-scale calculations that, in the center of the slab, we indeed re-

cover the behavior expected from macroscopic magnetostatics.

¹⁰J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975), Sec. 5.8; here we assume that χ is isotropic, and $\chi \ll 1$.

¹¹By symmetry, for the ideal C(111):H surface, $\vec{\sigma}$ is a diagonal tensor when expressed in basis vectors parallel and perpendicular to the surface. For an arbitrary surface, the off-diagonal elements are, in general, nonzero.

¹²We model the interaction of valence electrons with the ionic cores by norm conserving pseudopotentials (Ref. 13) in the Kleinman-Bylander form (Ref. 14). The wave functions are expanded in plane waves up to an energy cutoff of 70 Ry. For Brillouin zone integrations, we use 15 special \mathbf{k} points in the irreducible wedge of the Brillouin zone. To model the surface, a periodically repeated diamond slab of 20 C layers is used, with a (111) hydrogenated ideal surface at each side. The unit cell is hexagonal and contains twenty C atoms and two H atoms. The length of the hexagonal lattice constant a is equal to 2.503 Å, such that the C bond lengths in the center of the slab are equal to the computed bond length of bulk diamond (1.533 Å). After relaxing the slab by minimizing its total energy, the distance between the H and C layer is 1.116 Å. The distance between the first and second C layer contracts to 0.479 Å, which is 6% less than the corresponding bulk value. Negligible relaxations of less than 1% are observed for the deeper layers.

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²¹In principle, Eqs. (3) and (4) hold only in a finite system, since in an infinite solid σ_n^d and σ_n^p individually diverge due to the contributions at large r . However we have shown that the deviation of $\sigma_{||}(z)$ from its bulk value for a given atom originates from variations of the current density, $\Delta\mathbf{J}(\mathbf{r})$, localized around that same atom. This justifies an estimation of $\sigma(z) - \sigma(bulk)$ by means of Eqs. (3) and (4), with the spatial integrations restricted

to the vicinity of the atom for which $\sigma(z)$ is measured.

²²To this purpose we decompose $|\psi_{\text{surf}}^\Gamma\rangle$ in spherical harmonics Y_m^l inside the atomic spheres, where l and m are integer, $l \geq 0$, $-l \leq m \leq l$, and the axis of quantization $\hat{\mathbf{z}}$ is perpendicular to the surface. The surface possesses a 120° rotation symmetry about a $\hat{\mathbf{z}}$ axis intersecting the center of an atomic sphere. By this symmetry, the spherical harmonics coefficients of a nondegenerate eigenstate at the Γ point are zero, if $m \neq 3k$, where k is an integer. Furthermore, in carbon the spherical harmonics coefficients with $l > 2$ are known to be negligible, for states near the gap. Under this assumption, the only nonzero coefficients would be those with $m = 0$, i.e., $(\hat{\mathbf{n}}_\perp \cdot \mathbf{L})|\psi_{\text{surf}}^\Gamma\rangle = 0$. The density plot in Fig. 2 confirms this observation, since $|\psi_{\text{surf}}^\Gamma\rangle$ has the characteristic shape of a p_z (Y_0^1) state.